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MANUFACTURE OF SINTERED SILICON NITRIDES

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16. Abstract Sintered silicon nitrides are manufactured by sintering Si <sub>3</sub> N <sub>4</sub> powder containing 2-15 % in wt of a powder mixture composed of nitride powder of lanthanide or Y 100 parts and AlN powder less than 100 parts at 1500 - 1900 deg. temperature under a pressure of less than 200 Kg/ sq. cm. The sintered Si <sub>3</sub> N <sub>4</sub> has high mechanical strength in high temperature. Thus, Si <sub>3</sub> N <sub>4</sub> 93.0, Y 5.0 and AlN 2.0 % in weight were wet mixed in acetone in N atom, molded and sintered at 1750 deg. and 1000 Kg/sq. cm to give a sintered body having high hardness.					
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## DETAILS

### 1. Name of the invention

Manufacture of sintered silicon nitrides

### 2. Scope of the patent application

The manufacturing method of the sintered silicon nitrides according to this invention is characterized by the following: Silicon nitride powder containing 2 - 15 % in weight of the mixed substance consisting of 100 parts in weight of nitride powder which contains yttrium and lanthanum group elements and less than 100 parts in weight of aluminum nitride is sintered at 1500 - 1900 degrees temperature under the sintering pressure greater than 200 Kg/ square cm.

### 3. Detailed explanation of the invention

This invention concerns a method of manufacturing sintered silicon nitrides which are known to possess excellent characteristics at high temperatures.

Silicon nitride has been attracting attention as raw material for high temperature structural material such as gas turbine parts...etc. due to its mechanical strength and heat, impact and corrosion-resistance qualities. It is extremely difficult to obtain high density sintered material by attempting to sinter silicon nitride by itself. Therefore, a method to obtain sintered silicon nitride by sintering silicon nitride powder mixed with sintering agents such as magnesium, aluminum, yttrium or other powdered oxides

under normal or pressurized condition has been proposed in the past. However, sintered material obtained through the above method is not particularly suitable for high temperature structural material because of the following reason: Metallic substances contained within the oxides form silicate as the sintering agent reacts with silicon nitride, and the said silicate forms glass phases within the particle field of silicon nitride particles which form the sintered substance. At the time when the sintered material is subjected to high temperature, the mechanical strength of the material becomes significantly reduced because of softening of the glass phases. Accordingly, such material is not suitable for high temperature structural material.

The objective of this invention is to improve the above described method and provide a method to manufacture sintered silicon nitride whose mechanical strength will not deteriorate at high temperature.

According to the method of this invention, silicon nitride powder containing 2 - 15 % in weight of the mixed substance consisting of 100 parts in weight of nitride powder which contains yttrium and lanthanum group elements and less than 100 parts in weight of aluminum nitride is sintered at 1500 - 1900 degrees temperature under a pressure greater than 200 Kg/ square cm.

According to the method of this invention, sintered silicon nitride which is high density and which has small rate

of deterioration of mechanical strength at high temperature can be obtained. At the same time, such high density silicon nitride can be obtained even if the pressure level during the sintering process is kept relatively lower.

According to this invention, a mixture of nitride powder selected from the group consisting of yttrium and lanthanum and aluminum nitride is used as the sintering agent.

Examples of lanthanum group elements include lanthanum, cerium, neodymium, samarium, lutetium...etc. The most suitable among the ones listed above are lanthanum and cerium.

The volume of aluminum nitride per 100 parts in weight of elements selected from yttrium and lanthanum group elements should be less than 100 parts in weight, preferably 20 to 70 parts in weight. If the volume of aluminum nitride is too high, the particle phases of the sintered material become too great. In other words, the mechanical strength of the sintered material will be reduced.

The ratio of the sintering agent should be 2 to 15 % in weight, preferably 5 to 10 % in weight, of the total volume of the sintering agent and silicon nitride. If the volume of the sintering agent is extremely low, the sintered material will not have high mechanical strength at high temperature; if the volume of the sintering agent is extremely high, the mechanical strength of the sintered material will also be reduced due to excessive particle field phases within the

sintered material.

According to this invention, there is no limit to the method of mixing the silicon nitride powder which contains the sintering agent. The following methods may be used.

(1) The first method involves the removal of the organic solvent after mixing pre-mixed sintering agent (in powder form) and silicon nitride powder in the presence of an organic solvent such as acetone, benzine, toluene...etc. It is highly desirable to execute the above reaction in the atmosphere of dry inorganic gas because the sintered material by this invention tends to be sensitive to hydrolysis.

(2) According to the second method, a mixture of aluminum powder and powdered elements selected from a group of elements consisting of yttrium and lanthanum group elements is mixed with silicon nitride powder first. The mixture is heated to 750 - 1100 degrees C in the atmosphere of nitrogen gas in order to form nitrides of the above listed elements and aluminum. In this method, it is preferable to heat the said mixture to 550 - 900 degree C in the presence of hydrogen in order to remove oxygen contained within the mixture prior to bringing the mixture to the atmosphere of nitrogen gas.

The silicon nitride powder which contains sintering agent according to this invention may be sintered after molding of the powder is completed. In some instances, sintering and molding may be accomplished simultaneously.

According to the method by this invention, sintered

silicon nitride is obtained by heating the silicon nitride powder containing a sintering agent under pressurized condition.

The sintering pressure must be above 200 Kg/square cm. If the pressure level does not reach the required level, sintered substances high in mechanical strength cannot be obtained.

The sintering temperature should be 1500 - 1900 degrees C, preferably 1600 - 1800 degrees C. If the sintering temperature is lower than the lower margin of the recommended sintering temperature, sintered material cannot be expected to be mechanically strong. If the sintering temperature is higher than the upper margin of the recommended sintering temperature, silicon nitride will be dissolved.

Next, practical applications of this invention and comparative examples are shown. In these examples, the density of the sintered material is shown according to the Archimedean principle, and its hardness was measured using a QM type high temperature microscclermeter made by Nippon Kogakusha K. K. The flexural rigidity of the sintered material was measured by cutting a piece, 3 x 3 x 40 mm in size, out of the sintered material and by conducting a three point flexural rigidity test of the test piece under the condition of 20 mm span and 0.5 mm/minute cross head speed after polishing the surface of the test material. All % signs indicate % in weight.

## Practical application #1 and #2

Silicon nitride powder (nitrogen content of 38.2%, silicon content of 59.8%, oxygen content of 1.0%, comparative surface area of 7.8 sq. meters/ g) in the specific ratio listed in Tab. 1 and a sintering agent, a total of 10 g, and 10 ml of acetone were mixed together inside a ball mill made of alumina. The mixture was ground in nitrogen atmosphere for 16 hours at room temperature. The ground mixture was dried in the presence of nitrogen, and a powdery mixture was obtained once acetone was removed.

0.5 g of the powdery mixture was placed in a cylindrical container, 7 mm in diameter and 8 mm in height, and 1.5 ton/square cm of pressure was applied in order to form a molding. Once a molding was formed, it was moved into a capsule made of boron nitride, which was vacuum sealed inside a silica glass.

The double sealed molding described above was sintered under the pressure of 1000 Kg/sq. cm at the temperature indicated in Tab. 1 for 30 minutes. Density and hardness of the sintered material obtained in the manner described above are shown in Tab. 1.

## Comparison #1 and #2

The practical application #1 was repeated under the same conditions as the practical application #1 except the kind and



mixture ratio of the sintering agent and the temperature of sintering. The result is shown in Tab. 1.

#### Practical application #3 - #5

Silicon nitride powder (nitrogen content of 38.1%, silicon content of 60.2%, oxygen content of 1.4%, comparative surface area of 4.5 sq. meters/ g) in the specific ratio listed in Tab. 2 and a sintering agent, a total of 60 g, and 60 ml of acetone were mixed together inside a ball mill made of alumina.

The mixture was ground in nitrogen atmosphere for 16 hours at room temperature. The ground mixture was dried in the presence of nitrogen, and a powdery mixture was obtained once acetone was removed.

The powdery mixture was filled in a 40 mm x 20 mm mold made of graphite material, and 250 Kg/sq. cm of pressure was applied while it was hot pressed for one hour at the sintering temperature listed in Tab.2. In this manner, molding and sintering of the powdery mixture were completed simultaneously. Density and flexural rigidity of the sintered material obtained in this manner are shown in Tab. 2.

#### Comparison #3 - #5

The practical application #3 was repeated under the same conditions as the practical application #3 except the kind and

mixture ratio of the sintering agent and the sintering temperature. The result is shown in Tab. 2.

Key list for Tab. #1 and #2

a. mixture ratio    b. sintering temperature    c. density    d.  
flexural rigidity    e. hardness    f. practical application #  
g. comparison #

第 1 表 (Tab. 1)

	(a) 配 合 割 合 (b)							燒結溫度 (°C)	密 度 (g/cm <sup>3</sup> )	(e) 硬 度 (Kg/mm <sup>2</sup> )	
	Si <sub>3</sub> N <sub>4</sub>	YN	CeN	ALN	Y <sub>2</sub> O <sub>3</sub>	CoO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	(°C)	(g/cm <sup>3</sup> )	25°C	1200°C
(f) 實施例 1	95.0	5.0	0	2.0	0	0	0	1750	3.28	2100	810
" 2	92.0	0	5.0	3.0	0	0	0	1650	3.30	2050	790
(g) 比較例 1	92.9	0	0	0	4.8	0	2.3	1750	3.27	1950	200
" 2	92.0	0	0	0	0	5.0	3.0	1800	3.31	1920	120

第 2 表 (Tab. 2)

	(a) 配 合 割 合 (b)									燒結溫度 (°C)	密 度 (g/cm <sup>3</sup> )	(d) 曲 折 強 度 (Kg/mm <sup>2</sup> )	
	Si <sub>3</sub> N <sub>4</sub>	YN	LaN	CeN	ALN	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CoO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	(°C)	(g/cm <sup>3</sup> )	25°C	1200°C
(f) 實施例 3	93.0	5.0	0	0	2.0	0	0	0	0	1780	3.24	105	88
" 4	92.5	0	0	5.5	2.0	0	0	0	0	1760	3.28	95	83
" 5	92.7	0	5.3	0	2.0	0	0	0	0	1776	3.26	98	85
(g) 比較例 3	93.0	0	0	0	0	5.0	0	0	2.0	1780	3.25	93	62
" 4	92.7	0	0	0	0	0	5.3	0	2.0	1760	3.26	90	60
" 5	92.5	0	0	0	0	0	0	5.5	2.0	1770	3.29	92	53